Vapor-Phase Infrared and Raman Spectra and Ab-Initio Calculations of the Axial and Equatorial forms of Cyclohexane-d₁ and d₁₁

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Abstract

The vapor-phase infrared and Raman spectra of cyclohexane-d₁₁ in the C-H stretching region show two bands at 2,891 and 2,921 cm⁻¹ corresponding to the axial and equatorial C-H stretching modes respectively. Similarly, cyclohexane-d₁ has two C-D stretching modes at 2,145 and 2,164 cm⁻¹ [1] corresponding to the two forms. Force constants were calculated for these vibrations and these confirm the theoretical calculations, which show the equatorial bonds to be shorter and stronger. The force constant for the equatorial C-H stretching is 2% higher than for the axial.

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INTRODUCTION

The cyclohexane molecule in its lowest energy form exists in the chair conformation with D_{3d} symmetry. Its d_1 singly deuterated isotopomer has the unusual property that the C-D bond can either be axial or equatorial. Similarly, cyclohexane- d_{11} , which has only one 1H atom, has two distinct conformers where the C-H bond can be axial or equatorial. In 1984 Matrai and Gal [1] observed the C-D stretching bands for the d_1 vapor at $2,145\text{ cm}^{-1}$ (assigned to the axial) and $2,164\text{ cm}^{-1}$ (equatorial). The corresponding Raman bands for the liquid were at $2,144$ and $2,162\text{ cm}^{-1}$. In 1987 Gough and Murphy [2] reported the C-H stretching frequencies for the d_{11} isotopomer to be at $2,891\text{ cm}^{-1}$ for the axial form and $2,923\text{ cm}^{-1}$ for the equatorial. Numerous theoretical studies have been carried out on the conformations of cyclohexane [3-6]. These agree that the equatorial bond is shorter than the axial bond. In the present study we have recorded the vapor-phase infrared and Raman spectra of cyclohexane- d_{11} and also carried out theoretical calculations. From the spectra we calculated the force constants for the equatorial and axial C-H bonds and we correlated these to the calculated C-H bond distances.

EXPERIMENTAL

The sample of cyclohexane- d_{11} (98 atom % D) was purchased from CDN isotopes and was purified by trap-to-trap distillation. Infrared spectra were recorded using a Bruker Vertex 70 instrument, which was purged by a stream of dry nitrogen gas.

Raman spectra were recorded with a Jobin Yvon U-1000 spectrometer equipped with a charge-coupled device (CCD) detector with a resolution of 0.7 cm^{-1} . A Coherent Verdi V10 Nd:YAG laser operating at 532 nm and with 4W power at the sample was the excitation source. The vapor Raman spectra was recorded at 98°C. A special heatable Raman cell, which has been previously described [7,8], was utilized.

COMPUTATIONS

Structure calculations. The cc-pVTZ (triple- ζ) basis set was used with the second-order Møller-Plesset (MP2) *ab initio* method to calculate the energies and to compute the geometries of the conformations of cyclohexane. The Gaussian 09 program [9] was used for the computations, and the Semichem AMPAC/AGUI program [10] was used to visualize the structures.

Frequency calculations. The vibrational frequencies of the chair conformation of cyclohexane- d_1 and $-\text{d}_{11}$ along with their Raman intensities were calculated by using the Gaussian 09 program. The density functional theory (DFT) B3LYP method [11,12] was used with the cc-pVTZ basis set. The scaling factor of 0.961 was used for the vibrations of interest, based on previous work [13-18], which also has shown us that B3LYP/cc-pVTZ calculations do a better job than MP2/cc-pVTZ for reproducing vibrational frequencies.

RESULTS AND DISCUSSION

Figure 1 shows the vapor-phase infrared and Raman spectra of cyclohexane- d_{11} in the C-H stretching region. The two bands at 2,921 and 2,891 cm^{-1} clearly arise from the two conformational forms. Treating these vibrations with the harmonic oscillator model for a diatomic molecule allows us to calculate the force constants to be 4.646 mdynes/Å for the

equatorial C-H and 4.551 mdynes/Å for the axial C-H. Similarly, we can use the literature values [1] for the C-D stretching vibrations of cyclohexane-d₁ and we calculate force constants of 4.736 mdynes/Å for the equatorial form and 4.653 mdynes/Å for the axial form. These results are shown in Table 1. Ideally the force constants for the two isotopomers should be the same for the corresponding vibrations of the d₁ and d₁₁ molecules, but the calculations were carried out assuming the harmonic oscillator model for diatomic molecules. Hence, the anharmonicity has the effect of apparently increasing the force constant for the C-D stretching since the quantum states are deeper within the potential well. In addition, the C-D stretch being of lower frequency has increased coupling with the other vibrational modes. In any case, for the C-H stretch the force constant for the equatorial vibration is 2.1% higher than for the axial. For the C-D stretching it is 1.8% higher.

Figure 1. Vapor-phase infrared and Raman spectra of cyclohexane-d₁₁ in the C-H stretching region.

The calculated (DFT) B3LYP/cc-pVTZ frequency difference between the C-H axial and equatorial modes of 29 cm^{-1} ($2,921 - 2,892$) agrees almost perfectly with the observed difference of 30 cm^{-1} . For the C-D stretch of the d_1 molecule the reported experimental difference is 19 cm^{-1} [1] compared to our calculated difference of 23 cm^{-1} .

Table 1. C-H and C-D stretching frequencies, force constants and bond distance for cyclohexane- d_{11} and d_1 .

C-H stretching (d_{11})	Axial	Equatorial
Frequency (cm^{-1})	2891	2921
Force constant ($\text{mdyne}/\text{\AA}$)	4.551	4.646
Bond distance ($\text{\AA}$)	1.094	1.091
C-D stretching (d_1)		
Frequency (cm^{-1}) ^a	2145	2164
Force constant ($\text{mdyne}/\text{\AA}$)	4.653	4.736
Bond distance ($\text{\AA}$)	1.094	1.091

^aRef. [1]

Figure 2 shows the calculated C-H bond distance of the cyclohexane molecule in its chair, boat and twist-boat conformations. As can be seen, for the chair conformation, the equatorial C-H bond distances are shorter ($1.091\text{ \AA}$) than those for the axial C-H bonds ($1.094\text{ \AA}$). This is totally consistent with the calculated force constants which show the equatorial C-H bonds to be stronger. Figure 2 shows that the calculated *ab initio* MP2/cc-pVTZ C-H bond distances for the boat and twist-boat conformations also depend slightly on the position of the C-H bond, but not nearly as much as for the chair conformation. In our previous work on cyclopentane [19] we found that for the bent conformations the calculated *ab initio* CCSD/cc-pVTZ equatorial C-H bond length of $1.090\text{ \AA}$ is shorter than the axial bond length of $1.094\text{ \AA}$.

Figure 2. *Ab initio* MP2/cc-pVTZ calculated C-H bond distances of cyclohexane in its chair, boat, and twist-boat conformations.

CONCLUSIONS

It is interesting to note how isotopically substituted molecules can be invaluable for experimentally verifying the results of theoretical computations. Namely, they help to show that the equatorial C-H bonds of cyclohexane are stronger than the axial ones.

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Graphical Abstract